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Quantum Properties of Molecular Nanomagnets

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CNR CONSIGLIO NAZIONALE DELLE RICERCHE - ISTITUTO DI NANOSCIENZE -

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14. ABSTRACT
Multiple presentations and papers were submitted on the topic of exploiting molecular spin qubits in hybrid systems and coupling them to other superconducting qubits, spins/defects in semiconductors or any other solid state implementation of qubits applicable to Quantum Technologies.

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AOARD Scientific Project on Novel Nanomagnetic and Multifunctional Materials.

Title: *Quantum Properties of Molecular Nanomagnets (AOARD Project #134029)*

Collaborative project between:
Prof. Marco AFFRONTE, CNR- Institute NanoSciences Modena (and University of Modena e Reggio Emilia) Italy.
Prof. Stephen Hill, Florida State University and National High Magnetic Field Laboratory (USA)
Prof. Takeji Takui, Osaka City University (Japan)

SCIENTIFIC REPORT FOR ACTIVITIES IN 2016.

Coupling molecular spins to superconducting planar resonators.

Recently CNR started to investigate how molecular spins can be coupled to flying qubits such as microwave photons in superconducting circuits. The problem is relevant for Quantum Technologies since it may open the way to exploit molecular spin qubits in hybrid systems and eventually couple them to other superconducting qubits, spins/defects in semiconductors or any other solid state implementation of qubits. To create coherent dynamic, we need to achieve the *strong coupling regime* for which the coupling between spins and photons is stronger than decay rate of both the spin qubit and photons in resonant cavity. Since, in general, the coupling of magnetic dipole with magnetic component of the electromagnetic wave is weak such condition is hard to achieve. One strategy is to use spin ensemble in such a way that the coupling is effectively enhanced by a factor √N, being N the number of spins.

In 2015, CNR has demonstrated that electron spin ensembles of radicals coherently couple to microwave photons in high Tc YBCO planar resonator up to 50K and in finite magnetic field (***Applied Physics Letters*** 106, 184101 (2015); doi: 10.1063/1.4920930). This new research line has been pursued by CNR in 2016 in two ways:

-in a preliminary work (*Dalton Transactions* 45, 16596–16603 *(2016)* DOI: 10.1039/c6dt01953f) we have carried out systematic spectroscopic measurements looking for the coherent coupling between molecular magnetic centers and microwave photons. The aim was to find the optimal conditions and the best molecular features to achieve the strong coupling regime for which coherent dynamics of hybrid photons-spin state take place. To this end we used a high critical temperature YBCO superconducting planar resonator working at 7.7 GHz to investigate three molecular mononuclear derivatives, namely Cu(mnt)$_2$, [ErPc$_2$]$^-$TBA$^+$ and Dy-*trensal* and different organic radicals. Results are summarized in fig.1. The strong coupling regime was achieved for dense organic radical but not for diluted mono-nuclear samples. These results provide several hints on how to design molecular magnetic centers to be integrated into hybrid quantum circuits.

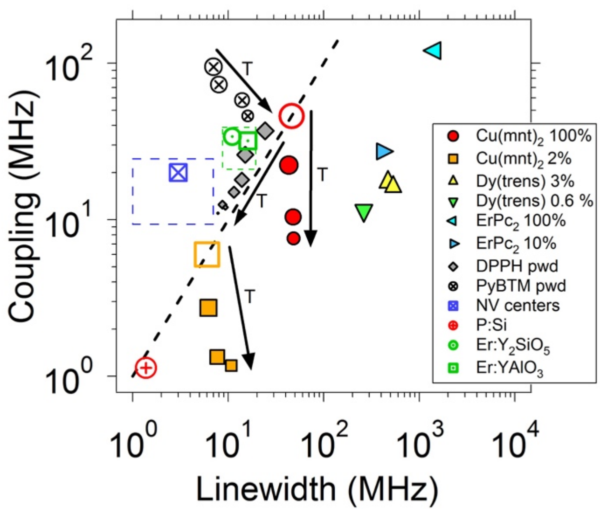

Figure 1 *Plot of coupling rate and spin linewidth parameters obtained by fitting the experimental data. Black arrows with T and the size of symbols represent the temperature evolution, from 2K (larger symbols) to 50 K (small symbols). The dashed line represents the threshold above which strong coupling regime is achieved.*

- In February 2016, Prof. T. Takui and Prof. Nakaza from OCU spent one week in Modena starting a new series of spectroscopic measurements on nitronil nitroxides radicals by YBCO planar MW resonators. Systematic investigation includes samples of both simple radical and bi-radical of different concentration. Data analysis which may account for the zero field splitting of the ground triple is still under way but these preliminary experimental spectra show that strong coupling regime can be achieved with non-concentrated samples, suggesting that exchange narrowing effect may significantly contribute at obtaining coherent spin photon states. These results will be subject of next coming joint publication.

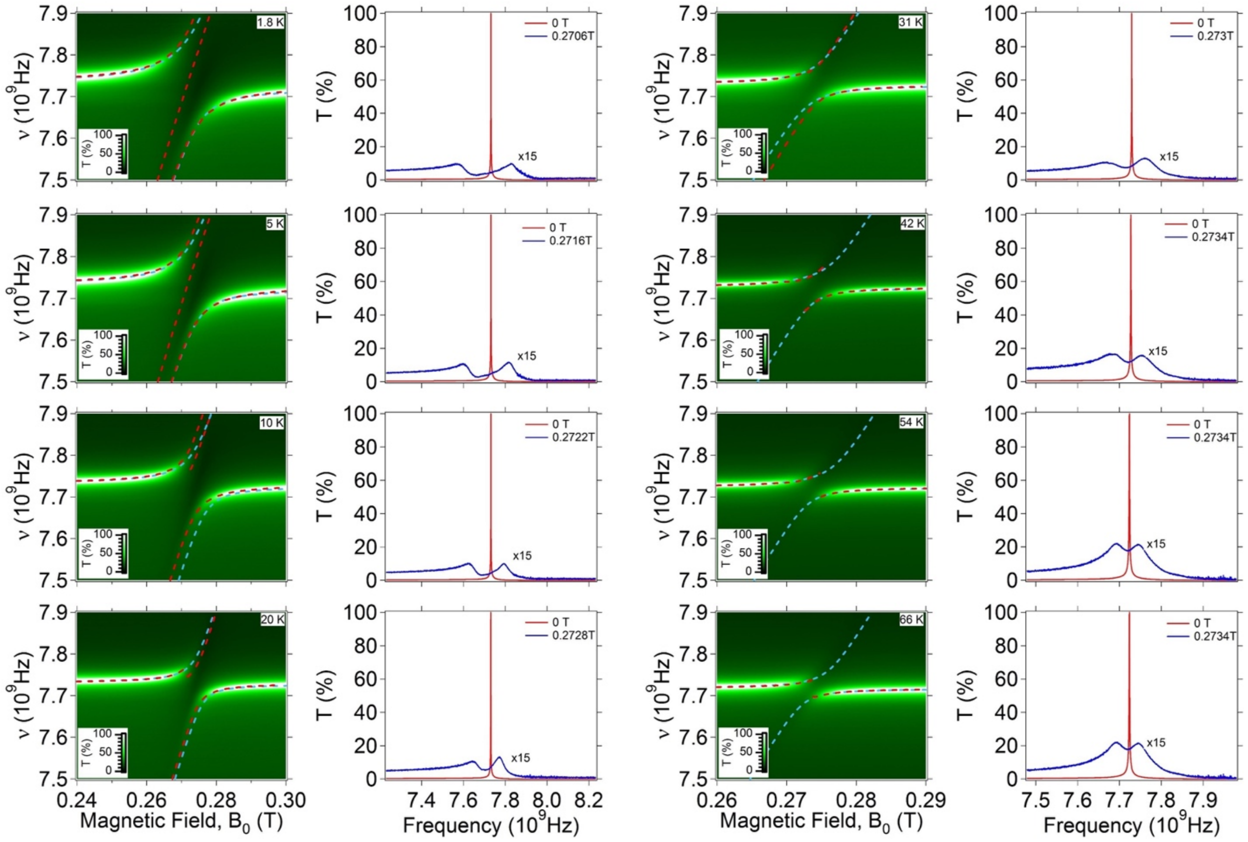

Figure 2 *Transmission spectral map for the IN-NO bi-radical measured at 2K and Pin = -15 dBm and comparison with simulated curves at the level anti-crossing.*

- in a further work we revisited the problem of coupling distinct ensembles of two level systems through photons in a quantum box by using organic radicals (spin 1/2) and a high T_c superconducting coplanar resonator with which an exceptionally strong coupling is obtained. Up to three spin ensembles are simultaneously coupled and are made physically distinguishable by chemically varying the Landé g factors and by exploiting the inhomogeneities of the applied magnetic field. The observed multiple anticrossing, along with the simulations performed within the input-output formalism, demonstrate the coherent coupling.

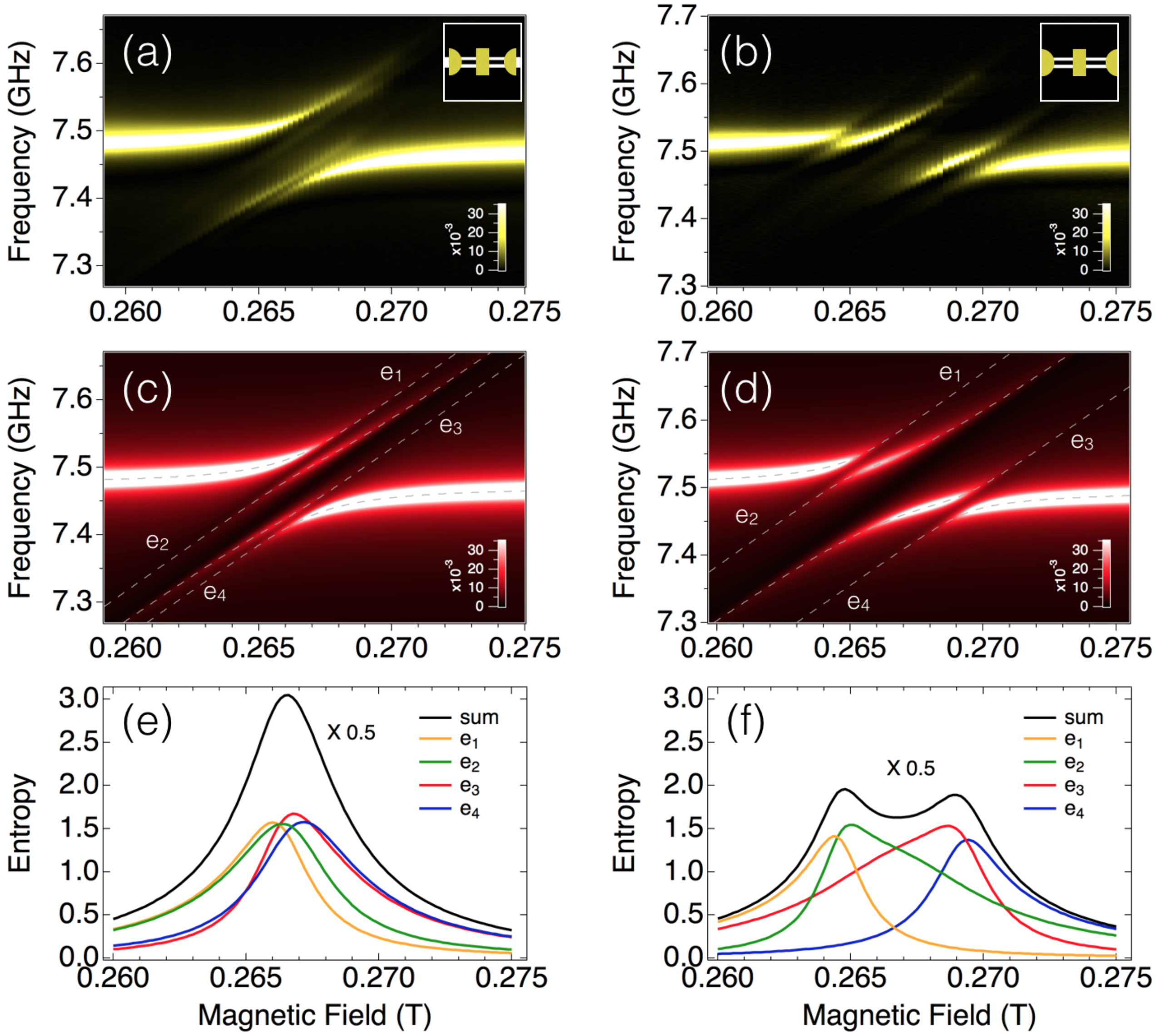

Figure 3: Transmission spectroscopy experiments with three spin ensembles. One ensemble is positioned at the center of the resonator, while the two external ensembles are placed on the edge of the central electrode (left column) or on the gap between the central strip and the external box (right column). In each column we display the experimental results obtained for a given geometry (a,b) and the corresponding simulations performed through the input-output formalism (c,d). Panels (e,f) show the entropic measures S_k, and their sum S calculated for the hybrid spin-photon modes, as a function of the magnetic field.

Electron Spin Resonance Experiments on Ln-Pc double and triple decker.

Lanthanide are appealing for electron spin manipulation since they have high and very anisotropic Landé *g*-factors. However, considering the ground state of most Ln, the intra-multiplet transitions are not allowed by conventional EPR selection rules. Few ESR experiments have been reported in literature on the molecular bricks*,* namely the bis(phtalocyaninato) lanthanide double-decker complexes ($LnPc_2$, Pc=phtalocyanine). In their neutral form, $LnPc_2$ complexes comprises an additional radical spin 1/2 delocalized onto the Pc molecules, which influences the low temperature magnetic properties and plays an important role when the molecule is coupled to our spintronic devices or deposited on a magnetic surface. The open question is to see whether the spin radical, which provides quite accessible EPR transitions, may give useful information when coupled to Ln in double and triple decker.

We (CNR) decided to get more insights on the role of this this spin radical by performing high frequency high field EPR experiments at National High Magnetic Field Laboratory in Tallahasse (FL, USA) exploiting the collaboration with group of Prof. S. Hill. Dr Alberto Ghirri (CNR researcher) and Claudio Bonizzoni (PhD student from University of Modena) have spent one month in June 2016 at NHMFL in Tallahasse. With the group of Prof S. Hill, they have carried out a systematic study by means of high frequency Electron Paramagnetic Resonance (EPR) spectroscopy on the series of $LnPc_2$ neutral compounds, where Ln=Tb, Dy, Ho and Er. Powder samples of $LnPc_2$ molecules were investigated by means of a multi-frequency transmission spectrometer operating at several frequencies in the range 25-400 GHz. The comparison with the EPR spectrum of YPc_2 shows that the resonances with *g*-factor near 2 are influenced by the presence of each Ln(III) ion (see Figure 2). We have investigated the frequency dependence of the resonance fields and compared these results with a theoretical model that includes the Ln-radical exchange interaction. For $TbPc_2$ the experimental results evidence that the coupling is ferromagnetic with an exchange constant of about $0.5 cm^{-1}$. This outcome is also corroborated by ab-initio calculations. These results provide hints for non conventional manipulation of Ln spins and will be subject of next coming joint publication.

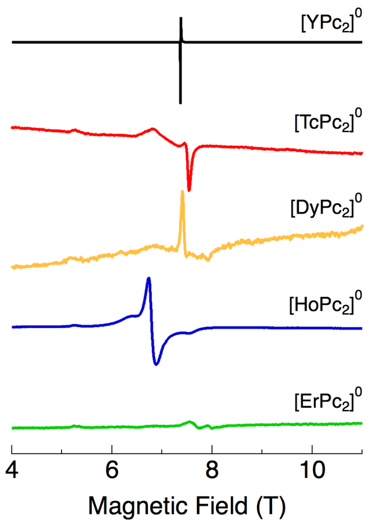

Figure 3: Comparison between the EPR spectra (frequency ≈210 GHz) taken on the series of $LnPc_2$ double-decker complexes at 2K.

On the same line of research, we performed X-ray experiments was to clarify how the magnetic interaction propagates from the lanthanide spin center through the phthalocyanines. We performed systematic X-ray absorption and dichroism investigation on $LnPc_2$ molecules sublimed on Ni(111) surface and on graphene grown on Ni. The lanthanide was changed from Tb to Dy and Er in order to appreciate the specific role of Tb. Results have been interpreted thanks to theoretical modelling. Overall they evidence: i) the role of d-orbitals to mediate interaction between the deep f-orbitals and the organic ligand in $LnPc_2$ ii) the role of graphene as decoupling layer avoiding complete charge

transfer; iii) the relay-like mechanism for magnetic coupling mediated by radical. (*Scientific Report 6,* 21740 *(2016), ACSnano* DOI: 10.1021/acsnano.6b04107 (2016)) Recently we had the opportunity to deepen these experimental investigations and to extend the study of interaction of prototypical molecules like CoPc and $LnPc_2$ (Ln=Tb, Dy, Er) with Ni substrate mediated by graphene with Au buffer layer.

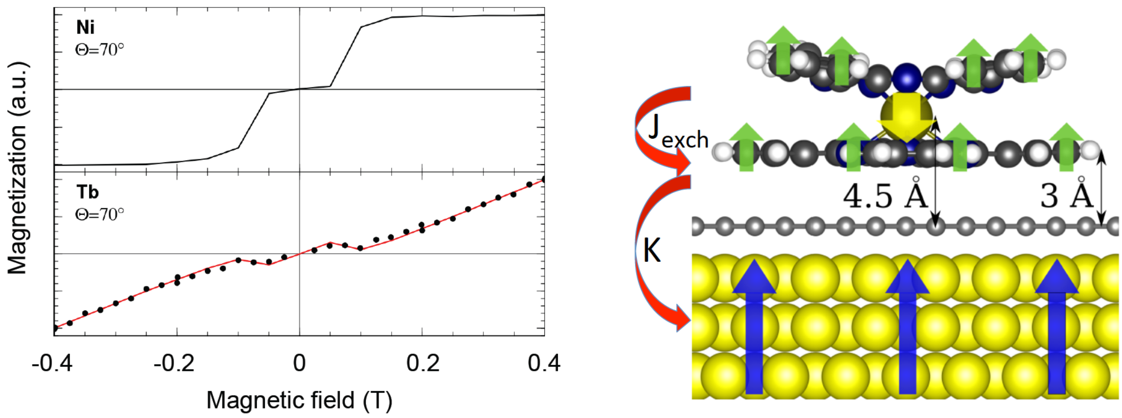

Figure 4 (left) X-ray magnetic dichroism on TbPc2 molecules deposited on magnetic Ni substrate. (right) sketch of our modelling and simulations.

VISITS.

- In February 2016, Prof. T. Takui and Prof. Nakaza from OCU spent one week in Modena.
- In June 2016-11-30 Dr Alberto Ghirri (CNR researcher) and Claudio Bonizzoni (PhD student from University of Modena) have spent one month in June 2016 at NHMFL in Tallahasse.
- In 18-19 November 2016 Prof. Stephen Hill visited our laboratory in Modena

PRESENTATION AT INTERNATIONAL CONFERENCES AND MEETINGS.

M. Affronte:
2016: oral presentation at ECMol Workshop on *Molecular Spintronics* Bologna, 17-19 November
2016: Invited Talks at Int. Workshop on 4th International Workshop on Novel Magnetic and Multifunctional Materials in Paris, France 4-8 July 2016
2015: 3 invited talks at Pacifichem Int Conf. , Honolulu (USA) 15-20 Dec.

A. Candini.
- European Materials Research Society, EMRS Fall Meeting, 19-22 September, Warsaw, Poland
"Graphene based devices for molecular spintronics" (Invited Talk)
European Physical Society, Condensed Matter Division, CMD26, 4-9 September 2016, Groningen, The Netherlands. "Bottom-up Graphene Nanoribbon devices with graphene electrodes" (Oral)
3rd Workshop on Surfaces, Interfaces and Functionalization Processes in Organic Compounds and Applications - SINFO III, 29-29 June 2016, Napoli, Italy. "Ultra high photoresponsivity with field effect control in a graphene nanoribbon device" (Oral)
Graphene 2016, 19-22 April 2016, Genova, Italy "Ultra high photoresponsivity with field effect control in a graphene nanoribbon device" (Oral)

A. **Ghirri.**
B. CMD26, Groeningen, The Netherlands, 4-9 September
C.

V. Bellini.
CMD26, Groeningen, The Netherlands, 4-9 September
Contributed talk: "Graphene-mediated exchange coupling between magnetic molecules and substrates: a DFT view"
EMRS Fall Meeting, Warsav, Poland, 19-22 September
Invited talk: "Graphene-mediated exchange coupling between magnetic molecules and substrates: a DFT view"
Contributed talk: "Relay-like exchange mechanism in the magnetic coupling between TbPc2 double decker molecules and Ni substrates"

F. Troiani: contributed talk at APS March Meeting Baltimora (March 2016).

RELEVANT PUBLICATIONS.

"Coherent Spin Dynamics in Molecular Cr8Zn Wheels"
Ghirri, Alberto; Chiesa, Alessandro; Carretta, Stefano; Troiani, Filippo; Van Tol, Johan; Hill, Stephen; Vitorica-Yrezabal, Inigo; Timco, Grigore; Winpenny, Richard; Affronte, Marco *J. Phys. Chem. Lett.*, 2015, 6 (24), pp 5062–5066 *DOI: 10.1021/acs.jpclett.5b02527*

YBCO microwave resonators for strong collective coupling with spin ensemble A. Ghirri, C. Bonizzoni, D. Gerace, S. Sanna, A. Cassinese, and M. Affronte ***Applied Physics Letters*** 106, 184101 (2015); doi: 10.1063/1.4920930

Coherently coupling distinct spin ensembles through a high-Tc superconducting resonator
A. Ghirri, C. Bonizzoni, F. Troiani, N. Buccheri, L. Beverina, A. Cassinese, and M. Affronte, **PHYSICAL REVIEW** A **93**, 063855 (2016)

Coupling molecular spin centers to microwave planar resonators: towards integration of molecular qubits in quantum circuits C. Bonizzoni, A. Ghirri, K. Bader, J. van Slageren, M. Perfetti, L. Sorace, Y. Lan, O. Fuhr, M. Rubene, and M. Affronte *Dalton Transactions (2016)* DOI: 10.1039/c6dt01953f

Heterodimers of Heterometallic Rings
Grigore Timco, Simone Marocchi, Elena Garlatti, Claire Barker, Morten Albring, Valerio Bellini, Franca Manghi, Eric J. L. McInnes, Wolfgang Wernsdorfer, Giulia Lorusso, Giuseppe Amoretti, Stefano Carretta, Marco Affronte and Richard E. P. Winpenny *Dalton Transactions* **45**, 16610-16615 *(2016)* DOI: 10.1039/c6dt01941b

A case study of anisotropic exchange interaction: Ln(III) bis-(phthalocyanine)s molecular nanomagnets on Ni substrate.
Candini, D. Klar, S. Marocchi, V. Corradini, R. Biagi, V. de Renzi, U. del Pennino, F. Troiani, V. Bellini, S. Klyatskaya, M. Ruben, K. Kummer, N. B. Brookes, H. Wende, M. Affronte *Scientific Report 6,* 21740 *(2016)*

Relay-like exchange mechanism between bis(phthalocyaninato) Terbium molecules and Ni(111) substrates across a graphene layer S. Marocchi, A. Candini, V. Corradini, R. Biagi, U. delPennino, M. Affronte, A. Soncini, V. Bellini. *ACSnano* DOI: 10.1021/acsnano.6b04107 (2016)